

## WEST Search History

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DATE: Tuesday, April 05, 2005

<b>Hide?</b>	<b>Set Name</b>	<b>Query</b>	<b>Hit Count</b>
		<i>DB=PGPB,USPT; PLUR=YES; OP=ADJ</i>	
<input type="checkbox"/>	L11	110 and (potassium or sodium)	45
<input type="checkbox"/>	L10	19 and (\$bromide or \$bicarbonate)	45
<input type="checkbox"/>	L9	16 and 18	47
<input type="checkbox"/>	L8	17 and (polymer\$ or oligomer\$)	31555
<input type="checkbox"/>	L7	\$triazine or PIPO	41488
<input type="checkbox"/>	L6	13 and 15	267
<input type="checkbox"/>	L5	14 and (sodium or potassium or calcium)	18160
<input type="checkbox"/>	L4	\$hypochlorite	18904
<input type="checkbox"/>	L3	12 and (ketone or aldehyde)	5010
<input type="checkbox"/>	L2	11 and (oxidat\$ or oxidiz\$ or oxidis\$)	6817
<input type="checkbox"/>	L1	unsaturated alcohol or allyl alcohol	17020

END OF SEARCH HISTORY

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=> d his

(FILE 'HOME' ENTERED AT 16:02:35 ON 05 APR 2005)

FILE 'REGISTRY' ENTERED AT 16:02:43 ON 05 APR 2005

L1 STRUCTURE UPLOADED

L2 50 S L1

L3 1293 S L1 FULL

FILE 'CAPLUS' ENTERED AT 16:04:02 ON 05 APR 2005

L4 1380 S L3

L5 8882 S ?UNSATURATED ALCOHOL? OR ?ALLYL ALCOHOL?

L6 307 S L5 AND (OXIDAT? OXIDIS? OR OXIDIZ?)

L7 135 S L6 AND (?KETONE? OR ?ALDEHYDE?)

L8 22199 S ?HYPOCHLORITE

L9 12884 S L8 AND (SODIUM OR POTASSIUM OR CALCIUM)

L10 4 S L7 AND L9

L11 4 S L7 AND L8

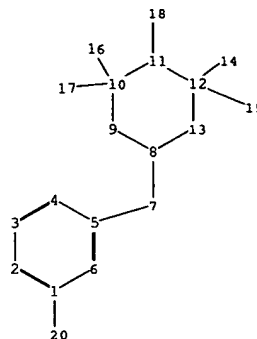
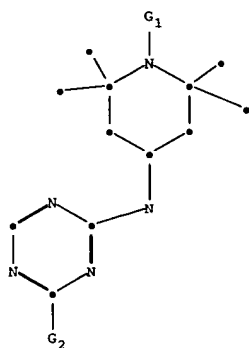
L12 44017 S ?TRIAZINE

L13 13 S PIPO

L14 1 S L12 AND L13

L15 1 S L11 AND L12

L16 1 S L7 AND L12



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chain nodes :
  7 14 15 16 17 18 20
ring nodes :
  1 2 3 4 5 6 8 9 10 11 12 13
chain bonds :
  1-20 5-7 7-8 10-16 10-17 11-18 12-14 12-15
ring bonds :
  1-2 1-6 2-3 3-4 4-5 5-6 8-9 8-13 9-10 10-11 11-12 12-13
exact/norm bonds :
  1-20 5-7 7-8 8-9 8-13 9-10 10-11 11-12 11-18 12-13
exact bonds :
  10-16 10-17 12-14 12-15
normalized bonds :
  1-2 1-6 2-3 3-4 4-5 5-6
isolated ring systems :
  containing 1 : 8 :

```

G1:H,O

G2:O,N

Match level :

```

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 8:Atom 9:Atom
10:Atom 11:Atom 12:Atom 13:Atom 14:CLASS 15:CLASS 16:CLASS 17:CLASS
18:CLASS 20:CLASS

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L10 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2003:610399 CAPLUS

DOCUMENT NUMBER: 139:164341

TITLE: A process for the oxidation of **unsaturated alcohols** to **aldehydes** and **ketones** by hypochlorites, using N-(2,2,6,6-tetraalkyl-4-piperidiny1-N-oxyl)-2-amino-1,3,5-triazine derivatives, e.g., Chimassorb 944 and 2020 N-oxyl derivatives such as PIPO, as catalysts

INVENTOR(S): Walther, Eric

PATENT ASSIGNEE(S): Firmenich SA, Switz.

SOURCE: PCT Int. Appl., 18 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003064362	A1	20030807	WO 2003-IB139	20030115
W: JP, US				
RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR				
EP 1472207	A1	20041103	EP 2003-734786	20030115
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, CY, TR, BG, CZ, EE, HU, SK				
US 2004064000	A1	20040401	US 2003-668790	20030922
PRIORITY APPLN. INFO.:			WO 2002-IB304	A 20020129
			WO 2003-IB139	W 20030115

OTHER SOURCE(S): CASREACT 139:164341; MARPAT 139:164341

AB The invention relates to the field of organic synthesis, and more precisely to a process for the synthesis of unsatd. **aldehydes** or **ketones** by oxidation of the corresponding unsatd. alcs. In particular, the oxidation is characterized by use of a **hypochlorite** salt and a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny1-N-oxyl)-2-amino-1,3,5-triazine derivative, preferably an N-oxyl derivative of the polymers

known under the trademarks Chimassorb 944 or Chimassorb 2020. A known example of such an N-oxyl derivative is the agent PIPO, which is an N-oxyl derivative of Chimassorb 944. Claims cover the oxidation of alcs. R1CH(OH)R2

[R1

= H, C1-20 linear, branched, or cyclic (un)saturated hydrocarbyl with optional substituents and/or replacement with 1-2 atoms of N or O; R2 = similarly described C2-20 alk(en/adien/atrien)yl group; or R1R2 forms a C5-20 unsatd. ring as described; substituents = C1-15 linear, branched, or cyclic alkyl, alkenyl, or aromatic] to corresponding **aldehydes** and **ketones** R1COR2, using hypochlorites M(OCl)<sub>n</sub> [M = alkali or alkaline earth metal; n = 2 or 1] and a catalytic amount of an oxyl derivative as described above. In contrast to prior art oxidns. of unsatd. compds. with hypochlorites, the new process gives characteristically high yields of desired products, as well as low yields of chlorinated byproducts (generally < 5%, frequently < 3%). In a general oxidation method, 1 equiv alc. in EtOAc containing 0.05 equiv PIPO and 0.01 equiv aqueous NaBr was

treated

with 1.1-1.45 equiv aqueous NaOCl containing 2 weight% added NaHCO<sub>3</sub>. After stirring

15-45 min, phase separation occurred, and the product was isolated by concentration

and bulb-to-bulb distillation For instance, 3-phenyl-2-propen-1-ol gave 99.5% conversion and 90% yield of 3-phenyl-2-propenal. In contrast, a

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literature method for the same reaction using a monomeric oxyl catalyst (4-methoxy-2,2,6,6-tetraalkylpiperidine-N-oxyl) gave only 79% conversion of alc. and 20% yield of **aldehyde**. In addnl. examples, conversions were typically 85-100% and yields were typically in the high range of 70-100%. Isophorone was prepared from isophorol in 87% conversion and 62% yield.